H-D EXCHANGE DURING SELECTIVE BENZENE HYDROGENATION TO CYCLOHEXENE

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INTRODUCTION

Ruthenium catalyzed hydrogenation of benzene to a mixture of cyclohexene and cyclohexane has been studied in gas phase (1-4) and slurry phase (5-9) reactions. The highest yields of cyclohexene, on the order of 30-40°%, have been observed in a four-phase slurry system consisting of a liquid benzene/cyclohexene/cyclohexane phase, an aqueous phase containing a dissolved transition metal salt, a solid heterogeneous ruthenium catalyst, and gas phase hydrogen. The presence of water and a transition metal promoter are generally required to achieve high selectivity to cyclohexene. There has been limited speculation on the role that water (1,2,4,8) and other promoters play in enhancing selectivity to cyclohexene. We have investigated the hydrogenation of benzene-d_6 with H_2 to probe mechanistic aspects of the four-phase slurry reaction. We have determined the extent of H-D exchange in the benzene feed and analyzed the H-D distributions in the products, cyclohexene and cyclohexane, at increasing benzene conversions.

EXPERIMENTAL

Benzene-d_6 hydrogenation was carried out in a 1 liter teflon-lined stirred reactor (Autoclave Engineers) at 150°C and 650 psig total pressure. A supported ruthenium catalyst (10) was reduced at 400°C in flowing hydrogen; a sample of the reduced catalyst was suspended in 150 cc of an aqueous solution of cobalt sulfate at 150°C in the teflon-lined reactor. Benzene-d_6 (250 cc) was preheated to 150°C and charged to the reactor. The total pressure was adjusted to 650 psig and maintained at 650 psig during hydrogenation. The reactor was sampled periodically and the organic phase composition determined by standard gas chromatographic methods. The H-D ratios and distributions in the organic components were determined by GC/MS.

RESULTS

Hydrogenation - Cyclohexene yield and selectivity vs. conversion are shown in Figure 1. Full conversion was reached after 100 minutes.

H-D Exchange in Benzene-d_6 - Less than 5% of the deuterium in benzene-d_6 was exchanged after 75 minutes (88% conversion). While the amount of hydrogen incorporated into the feed was very low, the amount increased as residence time in the reactor increased. The net make of benzene-h_6 increased from 0.2% after 11 minutes to 0.9% after 75 minutes.

H/D Ratios in Cyclohexane and Cyclohexene - The H/D ratios in the products, cyclohexane and cyclohexene, were determined at increasing benzene conversions by deconvolution and integration of the MS signals of the individual components. The ratios are shown in Table 1. We estimate that the error in these ratios is less than 5%. The expected ratios are 1.0 and 0.67 for cyclohexane ($C_6H_6D_6$) and cyclohexene ($C_6H_4D_6$), respectively, if one assumes no hydrogen incorporation by H-D exchange from H_2 or H_2O.

H-D Distributions in Cyclohexane and Cyclohexene - The distributions of H and D in cyclohexane and cyclohexene were determined by deconvolution of the GC/MS signals. The major products were $C_6H_6D_6$ and $C_6H_4D_6$; however there was significant scrambling of H and D giving the isotopic distributions shown in Figures 2 and 3.

DISCUSSION

Hydrogenation of benzene-d_6 was zero-order in benzene-d_6 up to 95% conversion; this is consistent with saturation of the catalytic sites with benzene-d_6. We were surprised to find no significant H-D exchange in the benzene-d_6 feed. This observation has two implications. First, it is unlikely that benzene adsorbs dissociatively. And second, cyclohexene disproportionation to benzene/cyclohexane does not occur to any measurable extent.

The data in Table 1 show that no H-D exchange occurred during hydrogenation of benzene-d_6 to cyclohexene and cyclohexane. However, the isotopic distributions in cyclohexane and cyclohexene (Figures 2 and 3) show that considerable *intermolecular* H-D exchange occurs *with conservation of deuterium*. The exchange of H and D between cyclohexene molecules to give the distributions observed supports the view that cyclohexene must adsorb and desorb numerous times so that the molecules can present both sides of the ring to the surface randomly. We believe that the key intermediate for the scrambling reaction is cyclohexene dissociatively adsorbed at the allylic position. As the reaction time in the reactor increases, the average residence time of the cyclohexene increases (it is continuously produced from benzene and continuously disappears as cyclohexane; thus, the residence time distribution of the cyclohexene molecules broadens as reaction time increases) and this results in increased scrambling with time as shown by the broadening of the distributions for cyclohexene in Figure 3. The less pronounced broadening of the cyclohexane distribution with time is consistent with little or no intermolecular exchange for the fully hydrogenated product; this is consistent with adsorption of cyclohexane being very weak relative to the adsorption strengths of benzene and cyclohexene.

The lack of a net hydrogen (H) incorporation into cyclohexene (or cyclohexane) is very surprising in view of the rampant scrambling that occurs. We believe that this is conclusive evidence supporting the view that the catalyst surface is hydrogen "starved" despite the very high hydrogenation rate (turnover frequency on the order of 10 sec^{-1} per exposed ruthenium site).

REFERENCES

1.   Don, J. A. and Scholten, J. J. F. Faraday Disc., Chem. Soc. 1982, 72, 145.
2.   van der Steen, P. J. and Scholten, J. J. F. Proceedings of the 8th International Congress on Catalysis 1984, 2, 659.

3. Schoenmaker-Stolk, M. C., Verwijs, J. W., Don, J. A., and Scholten, J. J. F. Appl. Catal. 1987, 29, 73.
4. van der Steen, P. J. and Scholten, J. J. F. Appl. Catal. 1990, 58, 281, 291.
5. Niwa, S., Mizukami, F., Isoyama, S., Tsuchiya, T., Shimizu, K., Imai, S., and Imamura, J. J. Chem. Tech. Biotechnol. 1986, 36, 236.
6. Niwa, S., Lopez Salinas, E., Mizukami, F., and Toba, M., Yukagaku 1989, 38(11), 938.
7. Niwa, S., Mizukami, F., Toba, M., Tsuchiya, T., Shimizu, K., and Imamura, J. Shokubai 1989, 31(6), 421.
8. Niwa, S. Mizukami, F., Imamura, J., and Itabashi, K. Sekiyu Gakkaishi 1989, 32(6), 299.
9. Nagahara, H., et al. US 4,734,536 (1988), JP 63-243038 (1988), JP 63-88139 (1988), all assigned to Asahi Kasei Kogyo K. K.
10. Details of catalyst preparation and characterization will be given in subsequent publications.

TABLE 1. H/D Ratios in Cyclohexane and Cyclohexene

Reaction Time, min	H/D, Cyclohexane	H/D, Cyclohexene
11	0.94	0.71
30	0.98	0.65
45	0.97	0.66
60	0.98	0.68
75	0.98	0.71
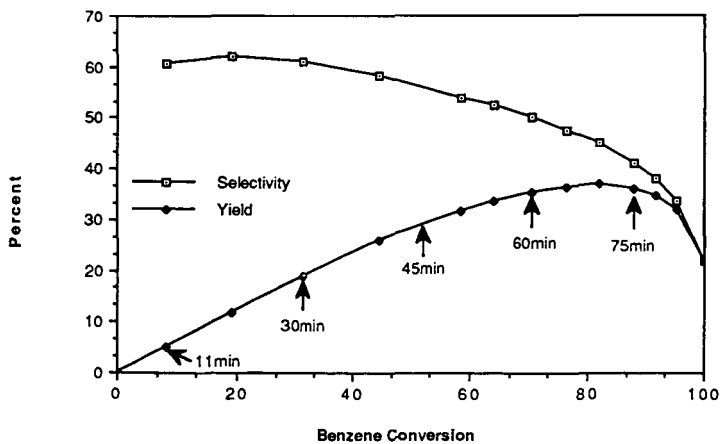
FIGURE 1. Cyclohexene selectivity and yield vs. benzene conversion. Note that the only products were cyclohexene and cyclohexane. The times noted correspond to the samples analyzed for H/D ratios and distributions.
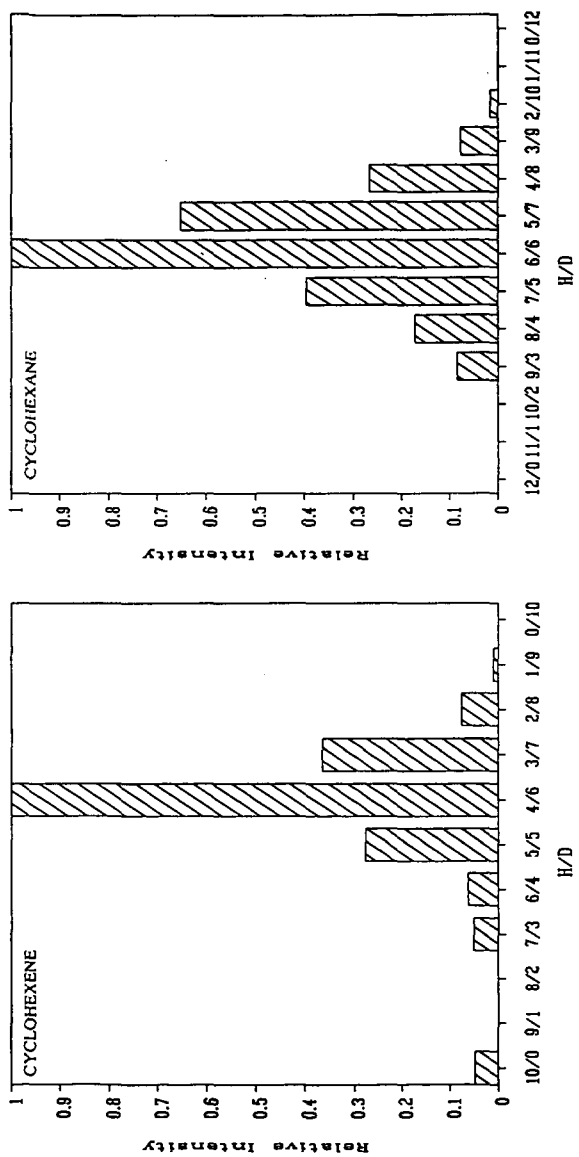
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FIGURE 2. Isotopic distributions in cyclohexane and cyclohexene; 11 min sample.
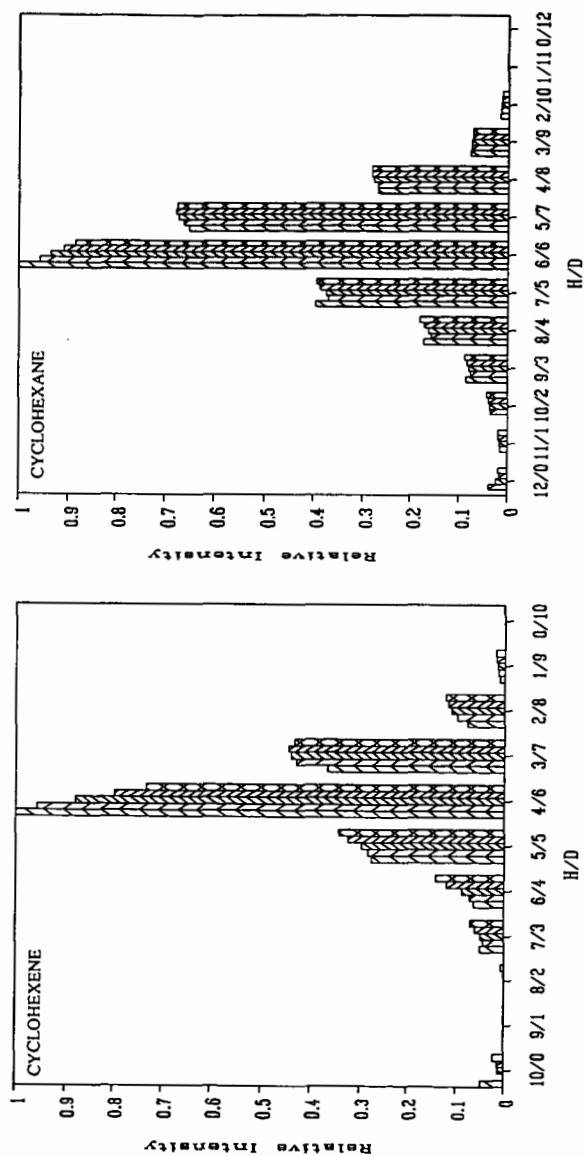
FIGURE 3. Isotopic distributions in cyclohexane and cyclohexene; reaction time increases from left-to-right (11, 30, 46, 60, 75 minutes) in each bar cluster.